

# Photoreduction of manganese oxides in seawater and its geochemical and biological implications

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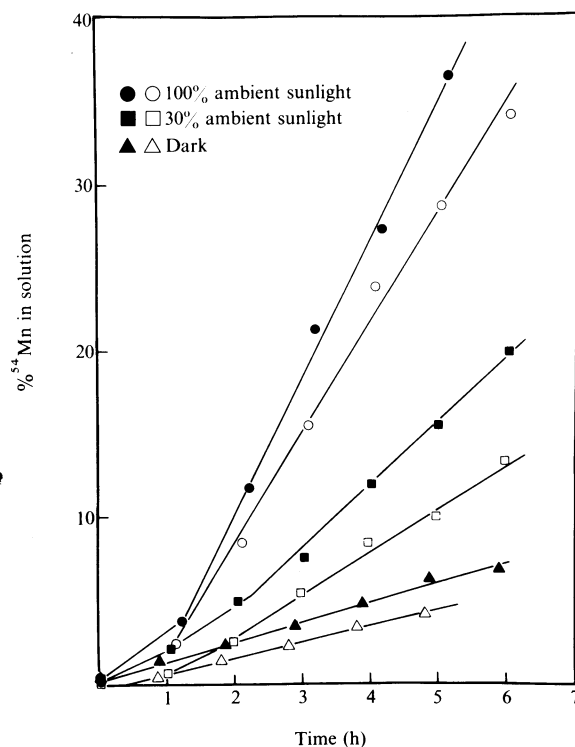
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Manganese is an essential micronutrient for all organisms. Its requirement by plants is particularly high because of its role in the oxidation of water in photosynthesis<sup>1-5</sup>. According to thermodynamic considerations, manganese should exist in oxic waters as  $\text{MnO}_2$  (ref. 6) which is insoluble and, therefore, not directly available for plant nutrition. In contrast to thermodynamic predictions, however, most of the manganese in near surface seawater exists as soluble reduced  $\text{Mn(II)}$  (ref. 7). Although slow oxidation kinetics are at least partially responsible for the presence of  $\text{Mn(II)}$  in oxic waters<sup>8,9</sup>, reduced manganese, nevertheless, should be converted to particulate manganese oxides (at rates that depend on several kinetic factors<sup>10,11</sup>) and be lost from the water column by sinking<sup>12</sup>. We report here experiments that demonstrate photoreduction of manganese oxides by dissolved organic substances (humic substances) in seawater. Such reactions appear to be important in maintaining manganese in a dissolved reduced form in photic waters, thereby enhancing its supply to phytoplankton.

Reduction of manganese oxide was investigated by measuring the dissolution of  $^{54}\text{Mn}$  oxides prepared from  $^{54}\text{MnCl}_2$  by permanganate oxidation<sup>13</sup>; oxides prepared by this procedure<sup>13</sup> have an approximate composition of  $\text{MnO}_{1.8}$ . Such mixed oxidation state oxides (referred to here as  $\text{MnO}_x$ ) are characteristic of those found in natural waters<sup>14</sup>. Experiments were conducted in coastal seawater, and in offshore seawater with and without additions of marine humic acids. Coastal water was collected near the mouth of the Newport River estuary, North Carolina, and was used within 2 h. Offshore near-surface seawater was collected<sup>15</sup> from the Gulf Stream off the North Carolina coast and was stored in the dark for either one week or two months before use. Marine humic acid (MHA) was isolated with Amberlite XAD-2 resin from seawater collected (5 m depth) 110 km south of Cape San Blas, Florida<sup>16,17</sup>.

Experiments were initiated by pipetting a suspension of  $^{54}\text{MnO}_x$  into 200-ml water samples to a final concentration of  $10^{-8} \text{ mol l}^{-1}$ . Samples in 250-ml Pyrex glass bottles were illuminated with either sunlight attenuated to different intensities or light from a bank of fluorescent bulbs. Samples of 10–20 ml were withdrawn hourly and filtered through 0.2  $\mu\text{m}$  pore size Nuclepore filters, which quantitatively retained the  $\text{MnO}_x$ . Filtrate were measured for  $^{54}\text{Mn}$  by  $\gamma$ -ray scintillation counting. The percentage of  $\text{MnO}_x$  dissolution was computed from the amount of  $^{54}\text{Mn}$  in the filtrate relative to that added to the samples.

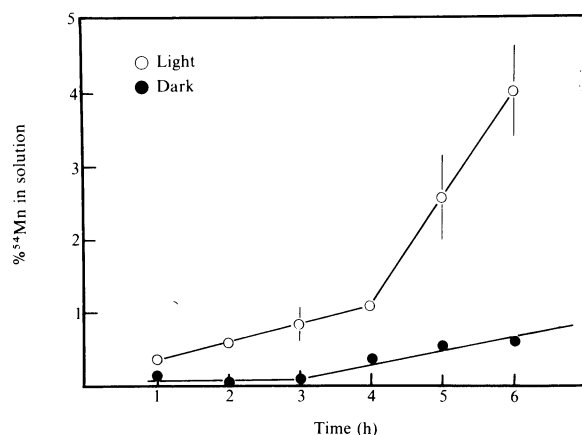
At least some  $\text{MnO}_x$  dissolution occurred with time in all samples. Rates of dissolution increased considerably with increasing light intensity (Figs 1–4) and with the addition of MHA (Figs 3, 4). Dissolution was a linear function of time in the dark provided the samples contained  $1 \mu\text{mol l}^{-1} \text{ MnCl}_2$ , which was added to displace newly formed  $^{54}\text{Mn}^{2+}$  from adsorption sites on  $\text{MnO}_x$  (ref. 14). Because of this displacement, the amount of  $^{54}\text{Mn}$  in solution with time was higher in samples containing added  $\text{MnCl}_2$  (Fig. 1). Rates of  $^{54}\text{MnO}_x$  dissolution increased with time for samples exposed to light, but approached constant rates after 1–4 h depending on the sample, the light source and intensity, and whether or not  $\text{MnCl}_2$  had been added. The final rates of  $^{54}\text{MnO}_x$  dissolution in coastal seawater samples exposed to full sunlight were about 7–8 times



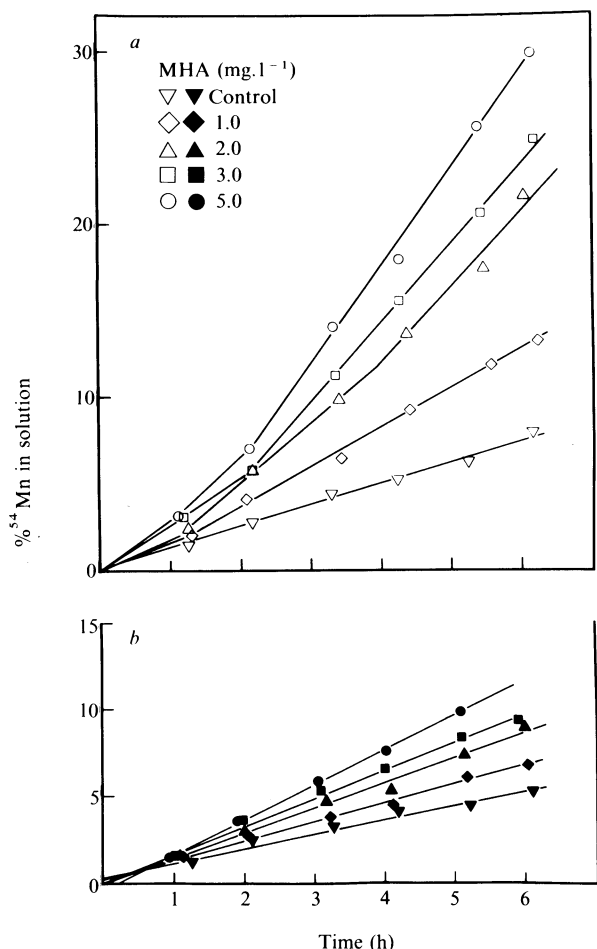
**Fig. 1** Dissolution of  $^{54}\text{MnO}_x$  in 35% coastal seawater at pH 8.1 and 21 °C. Samples were illuminated with ambient sunlight on a partially cloudy day ( $500\text{--}2,000 \mu\text{E m}^{-2} \text{ s}^{-1}$ ) and with sunlight attenuated to 30% with neutral density screens. Bottles were wrapped in aluminum foil for dark subsamples. Closed and open symbols are for subsamples with and without  $1.0 \mu\text{mol l}^{-1} \text{ MnCl}_2$  respectively.

higher than rates for samples in the dark. Similar rates were observed in filtered (0.2  $\mu\text{m}$  pore size Nuclepore) and unfiltered coastal seawater in preliminary experiments, indicating that dissolved rather than particulate substances are responsible for  $\text{MnO}_x$  dissolution.

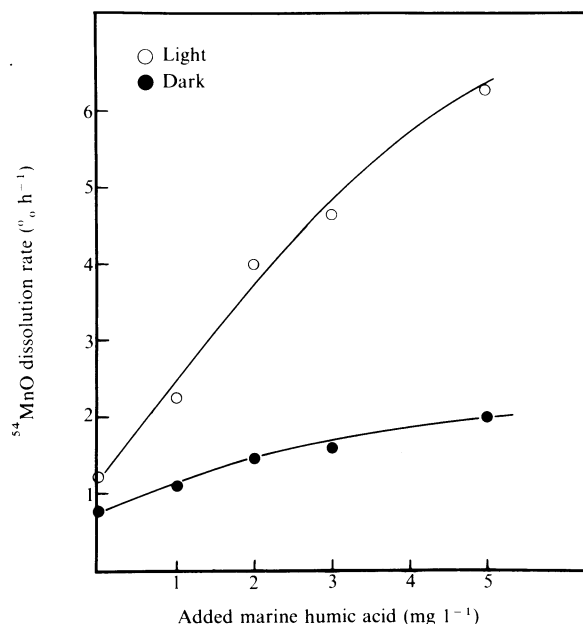
Since manganese oxides are insoluble, their photo-enhanced dissolution must proceed through a change in oxidation state. Both reduced manganous ions,  $\text{Mn}^{2+}$ , or permanganate ions,  $\text{MnO}_4^-$ , are highly soluble, but the presence of oxidizing agents sufficiently strong to oxidize  $\text{MnO}_x$  to  $\text{MnO}_4^-$  is unlikely in seawater. On the other hand, seawater contains a wide spectrum



**Fig. 2** Dissolution of  $^{54}\text{MnO}_x$  in 36%, pH 8.2 Gulf Stream seawater stored in a 50 l polyethylene carboy in the dark at 4 °C for 1 week. Illumination was provided by natural sunlight ( $2,000 \mu\text{E m}^{-2} \text{ s}^{-1}$ ) on a sunny day. Experimental temperature was 18 °C. Error bars indicate the range for two replicates.



**Fig. 3** Effect of marine humic acids (MHA) on the dissolution of  $^{54}\text{MnO}_x$  in 2-month old Sargasso seawater at  $20^\circ\text{C}$  and pH 8.1. All samples contained  $1.0\ \mu\text{mol l}^{-1}$   $\text{MnCl}_2$  to help facilitate desorption of reduced  $^{54}\text{Mn}^{2+}$ . *a*, Open symbols are for samples exposed to light ( $290\ \mu\text{E m}^{-2}\text{s}^{-1}$ ) from fluorescent bulbs (Vita-Lite, Duro-test Corp.). *b*, Closed symbols are for parallel samples maintained in the dark.



**Fig. 4** Effect of MHA addition on the final linear rates of  $^{54}\text{MnO}_x$  dissolution in Sargasso seawater. Rates were determined from data plotted in Fig. 3. Rates for samples exposed to light are for the time interval 2–6 h. Those for dark samples are for the interval 1–6 h.

of dissolved organic compounds<sup>18</sup>, many of which are reasonably strong reducing agents: several organic compounds including ascorbic acid, gallic acid, and tannic acid reduce  $\text{MnO}_x$  to soluble  $\text{Mn}^{2+}$  (refs 14, 19). We have demonstrated that a major class of organic compounds in seawater, humic acids, greatly enhance  $\text{MnO}_x$  dissolution. Similarly, in other experiments, we found that humic and fulvic acids present in river water also bring about  $\text{MnO}_x$  dissolution and that this reaction is also strongly stimulated by light.

From the above evidence, it seems that the dissolution of  $\text{MnO}_x$  in seawater results from its reduction to  $\text{Mn}^{2+}$  by organic compounds such as humic acids. Enhancement of this dissolution by light is apparently due to the photoactivation of organic compounds that are either dissolved or adsorbed onto  $\text{MnO}_x$  surfaces. Photoactivated reduction of other transition metals,  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ , by carboxylamine ligands is well documented<sup>20,21</sup>. Of more direct relevance here, however, is the observation that iron is reduced from the ferric to the ferrous state by natural humic substances<sup>22</sup>. This reaction, like the dissolution of  $\text{MnO}_x$ , is strongly stimulated by light.

Light activated dissolution of manganese oxides can at least partially explain the unusual vertical distributional pattern of manganese in the ocean. Unlike other trace metals (such as Cu, Zn, Cd, and Ni) whose concentrations increase with depth due to biological scavenging at the surface and regeneration at depth<sup>22</sup>, manganese profiles usually show a pronounced maximum in the photic zone<sup>23–26</sup>. For example, manganese concentrations in ocean waters of the California Current decrease by 5–10-fold in the depth interval 50–100 m (ref. 7). Furthermore, only ~1% of the manganese in the upper 25 m is in a particulate form. As dissolved manganese concentrations decrease sharply near the bottom of the photic zone, particulate concentrations increase to values of up to 30% of the total manganese.

We suggest that the surface maxima in manganese concentrations in the sea are due to two important factors: (1) high input rates to surface waters from continental sources via aeolian and riverine transport<sup>27</sup>; and (2) photoactivated reduction of manganese oxides to  $\text{Mn}^{2+}$ . The importance of the latter process would be to dissolve manganese oxides entering the surface of the ocean (for example, as oxide coatings on minerals) and to prevent appreciable oxidation of dissolved  $\text{Mn}^{2+}$  to particulate manganese oxides which, through sinking, would be lost from the water column. In surface waters there is an abundance of light and a relative abundance of dissolved organic matter derived directly or indirectly from photosynthesis. In these waters, photoactivated reduction by dissolved organic compounds would redissolve newly formed manganese oxides, explaining the overwhelming predominance of dissolved over particulate manganese in surface seawater. Due to decreases in both light and dissolved organic matter with depth, manganese oxides formed in seawater below the photic zone would be far less likely to be redissolved by reduction, and the formation of such oxides would explain the increase in particulate manganese near the bottom of the photic zone. The sinking of these particles, in turn, would appreciably contribute to the sharp decrease in manganese concentrations with depth below the photic zone.

Because of its requirement in photosynthesis, the availability of manganese in surface waters can have considerable biological importance. For example, deep seawater that is upwelled to the surface often contains insufficient manganese to support maximum plant growth<sup>28–30</sup>. From the above discussion, it appears that photoreduction of manganese oxides by dissolved organic compounds is an important process in the solubilization and retention of manganese in the photic zone, thereby, helping to maintain an adequate supply of manganese to phytoplankton. Since the ultimate source of the organic reducing agents (such as humic acids) is the biological community itself, the production of such compounds can be viewed as a biological conditioning of surface seawater which helps facilitate maximum primary

productivity in the sea. More specifically, the photochemical reduction of manganese oxides by those compounds appears to constitute a set of external photochemical reactions that enhances the supply of manganese required in the internal photochemical reactions of photosynthesis.

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